



Formation of disinfection by-products in the ultraviolet/chlorine advanced oxidation process



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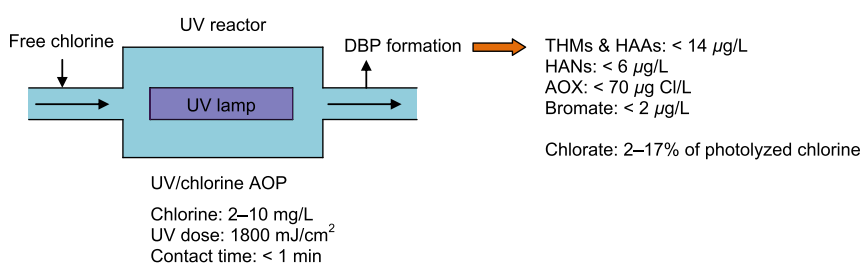
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HIGHLIGHTS

- UV/chlorine leads to low organic DBP formation for a <1 min reaction time.
- HAN formation was fast, but overall concentration was below 6 µg/L.
- UV/chlorine increases 24 h DBP formation potential to the same extent as UV/H₂O₂.
- Chlorine photolysis leads to low bromate formation of less than 2 µg/L.
- Approximately 2–17% of photolyzed chlorine converts to chlorate.

GRAPHICAL ABSTRACT



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ABSTRACT

Disinfection by-product (DBP) formation may be a concern when applying ultraviolet light and free chlorine (UV/chlorine) as an advanced oxidation process (AOP) for drinking water treatment, due to typically large chlorine doses (e.g. 5–10 mg L⁻¹ as free chlorine). A potential mitigating factor is the low chlorine contact times for this AOP treatment (e.g. seconds). Full-scale and pilot-scale test results showed minimal trihalomethane (THM) and haloacetic acid (HAA) formation during UV/chlorine treatment, while dichloroacetonitrile (DCAN) and bromochloroacetonitrile (BCAN) were produced rapidly. Adsorbable organic halide (AOX) formation was significant when applying the UV/chlorine process in water that had not been previously chlorinated, while little additional formation was observed in prechlorinated water. Chlorine photolysis led to chlorate and bromate formation, equivalent to approximately 2–17% and 0.01–0.05% of the photolyzed chlorine, respectively. No perchlorate or chlorite formation was observed. During simulated secondary disinfection of AOP-treated water, DBP formation potential for THMs, HAAs, HANs, and AOX was observed to increase approximately to the same extent as was observed for pretreatment using the more common AOP of UV combined with hydrogen peroxide (UV/H₂O₂).

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1. Introduction

Under certain conditions, an advanced oxidation process using ultraviolet light combined with free chlorine (UV/chlorine AOP) has been shown to have comparable efficiency to a similar AOP using UV/hydrogen peroxide (H₂O₂) for the destruction of organic contaminants in water treatment (Wang et al., 2012; Watts and Linden, 2007; Watts et al., 2007). However,

almost all work with UV/chlorine has been conducted in the laboratory, with only one full-scale drinking water treatment process known to the authors (the Middleton Water Supply System, Canada) (Wang et al., 2011). One of the concerns associated with UV/chlorine treatment is the need for relatively high chlorine doses relative to conventional drinking water chlorination (e.g. 5–10 mg L⁻¹ vs. 0.2–2 mg L⁻¹ as free chlorine) (Wang et al., 2012; Watts et al., 2007). It is hypothesized that this could promote the formation of chlorinated by-products (conventionally referred to as disinfection by-products, DBPs). A possible mitigating factor is that chlorine contact times during UV/chlorine treatment could be in

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the order of seconds because of the rapid and almost complete chlorine photolysis expected in the UV reactor (Wang et al., 2011). In contrast, DBP formation in chlorine disinfection is normally associated with hours of contact time. The formation of DBPs associated with chlorination has been widely studied, but little information is available on the unique high dose/short contact time conditions that would occur during UV/chlorine treatment. UV/chlorine photolysis also leads to the formation of the chlorine radical ($\bullet\text{Cl}$), which may react with natural organic matter (NOM) to form chlorinated DBPs. This has not been experimentally confirmed, although a study reported by Fang et al. (2014) indicated that $\bullet\text{Cl}$ played an important role in the destruction of benzoic acid in a UV/chlorine AOP under laboratory conditions. Chlorine photolysis may also directly produce inorganic DBPs of possible health concern, such as perchlorate (ClO_4^-), chlorate (ClO_3^-), and chlorite (ClO_2^-) (Buxton and Subhani, 1972; Feng et al., 2010; Kang et al., 2006), as well as bromate (BrO_3^-) in the presence of bromide (Br^-) (von Gunten and Hoigné, 1994).

The potential impact of UV/chlorine treatment on DBPs includes not only DBPs that may form during the treatment, but also the possible effect on organic precursors that may subsequently react with chlorine on secondary chlorination. Previous studies on the impact of UV/ H_2O_2 pretreatment on subsequent THM and HAA formation have suggested that such an effect is, in part, AOP-dose specific. Low and moderate AOP doses (e.g., UV doses in the order of up to 1000 mJ cm^{-2}) have been observed to lead to enhanced THM/HAA formation on subsequent chlorination (Dotson et al., 2010; Kleiser and Frimmel, 2000), while THM and HAA formation following higher AOP doses (UV of $3500\text{--}5000 \text{ mJ cm}^{-2}$) have been observed to be decreased (Toor and Mohseni, 2007; Liu et al., 2002).

There has been only a limited number of studies to date on DBP formation following UV/chlorine treatment, most of which have reported some formation of organic chlorinated DBPs during the AOP and/or in subsequent secondary chlorination (Liu et al., 2006; Pisarenko et al., 2013; Weng et al., 2012; Deng et al., 2014; Shah et al., 2011). None of these studies have simulated the conditions that would be expected to occur in a plant, that is high free chlorine doses ($5\text{--}10 \text{ mg L}^{-1}$ as free chlorine), high UV doses ($>1000 \text{ mJ cm}^{-2}$), but short reaction times ($<1 \text{ min}$). This research addresses such conditions, as well as the impact of the AOP treatment on subsequent secondary chlorination DBP formation. The work was conducted at full-scale using a medium pressure (MP) UV reactor with a treatment capacity of 8.6 MLD, as well as using a pilot-scale batch MP UV reactor with a volume of 40 L. The impact of UV/chlorine treatment on DBPs was also compared to parallel treatment using the more conventional UV/ H_2O_2 AOP.

2. Material and methods

2.1. Experimental procedures

2.1.1. Full-scale experiments

Full-scale experiments were conducted at the City of Cornwall Water Purification Plant (Ontario, Canada). The plant draws water from the St. Lawrence River and treats it using prechlorination, alum coagulation, flocculation, settling, conventional sand/anthracite filtration, and UV disinfection. The water quality after the post-filtration stage is summarized in Table 1. Following filtration, Trojan MP UVSwift 8L24 UV reactors are used for primary disinfection as well as for UV/ H_2O_2 advanced oxidation during periods of taste and odor problems, which historically occur in late summer. One UV unit was isolated for this study, and operated with its 100 L s^{-1} flow going to waste (shown in Fig. 1).

The full-scale study involved treating the flow with chlorine alone at three doses (2, 6, and 10 mg L^{-1} as free chlorine), UV alone, UV/chlorine (2, 6, and 10 mg L^{-1}), UV/ H_2O_2 (1.0, 2.9, and $4.8 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$, the same molar concentrations as chlorine), and at three pH levels (6.5, 7.5, and 8.5). Sodium hypochlorite (NaOCl) stock solution (12.5 wt.%, NSF 60 certified, Olin Chlor Alkali) or H_2O_2 stock solution (35 wt.%, NSF 60 certified, Arkema Inc.), provided by the Cornwall plant, was injected between the filters and the UV reactors. The travel time between chemical

Table 1
Full- and pilot-scale post-filtration water quality parameters.

Test	Cornwall—early April	Cornwall—late May	Pilot-scale
Source	St. Lawrence River	St. Lawrence River	Lake Simcoe
Temperature ($^{\circ}\text{C}$)	3	12	7–11
pH	8.1	7.9	7.5
Turbidity (NTU)	0.04	0.02	0.2
Alkalinity ($\text{mg CaCO}_3 \text{ L}^{-1}$)	85	92	123
TOC (mg C L^{-1})	1.6	1.5	3.5
Absorbance at 254 nm (cm^{-1})	0.02	0.02	0.04
Chlorine residual (mg L^{-1} as free chlorine)	0.3	0.1	0

injection immediately downstream of the filter and the UV reactor effluent was determined by tracer tests to be approximately 30 s at the flowrate of 100 L s^{-1} . The UV dose from 200 to 400 nm for all treatment conditions was estimated to be approximately $1800 \pm 100 \text{ mJ cm}^{-2}$, based on the chlorine photolysis rate determined by Wang et al. (2012). The actual UV dose may deviate from this value because the water matrix and UV reactor used here are different from those used by Wang et al. (2012). DBP formation by UV/chlorine, however, was compared to that by UV/ H_2O_2 under parallel conditions, so the actual UV dose is not required to make this comparison. pH adjustment was achieved by the addition of 10% (w/w) sulfuric acid (H_2SO_4) or 1.5% (w/w) sodium hydroxide (NaOH) through injection ports beside the chlorine or H_2O_2 injection port. Once the desired pH value was achieved, it was found to be very stable in all trials.

The DBPs that were monitored are listed in Table 2. DBP samples were collected downstream of the UV reactor with simultaneous quenching of residual free chlorine using (i) 200 mg L^{-1} sodium sulfite (Na_2SO_3) for THMs (Farré et al., 2011), HAAs (Li et al., 2014), and AOX (followed by acidification to $\text{pH} < 2$) (Crebelli et al., 2005), (ii) $50 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ for HANs, HKs, and CP (Shams El Din and Mohammed, 1998) with addition of phosphate buffer to $\text{pH} 4.8\text{--}5.5$ (USEPA, 1995), and (iii) 50 mg L^{-1} ethylenediamine for inorganic DBPs (USEPA, 1997). It is noted that ammonium chloride was not used as a dechlorinating agent in this study, because it was shown to lead to an overestimation of HAAs by Hong et al. (2007, 2008). Our preliminary results (data not shown) also indicated that ammonium salts could lead to a small but significant overestimation of THMs, HAAs, HANs, and AOX. In contrast, we found that Na_2SO_3 was appropriate for THM, HAA (except for MBAA, which was typically negligible), and AOX samples, and H_2O_2 was appropriate for HAN samples. DBPs that were measured immediately after the UV reactor represented 30 s of chlorine contact time. In addition, the water downstream of the reactor that had been treated with UV alone and UV/chlorine at the maximum chlorine dose (i.e. 10 mg L^{-1}) was dosed with additional chlorine to reach 6.5 mg L^{-1} as free chlorine (an arbitrarily 'high' amount), and then subjected to DBP formation potential (DBP-FP) tests for 24 h at room temperature, according to a modified uniform formation condition test (Summers et al., 1996). DBP-FP following UV/ H_2O_2 treatment at $4.8 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ was also tested, but 0.2 mg L^{-1} catalase from bovine liver (powder, 2000–5000 units/mg protein, Sigma-Aldrich) was added to samples to quench the residual H_2O_2 before dosing with 6.5 mg L^{-1} chlorine (Liu et al., 2003). The purpose of these formation potential tests was to observe the impacts of the UV, UV/chlorine, and UV/ H_2O_2 pretreatments on subsequent chlorination DBP formation.

2.1.2. Pilot-scale experiments

Pilot-scale experiments were carried out in a 40 L Rayox® completely-mixed batch reactor (Model: PS1-1-120, Calgon Carbon Corporation, Pittsburgh, USA) equipped with a 1 kW MP lamp (Heraeus Noblelight GmbH, Germany) (shown in Fig. 1) to simulate the UV and chemical oxidant doses applied at Cornwall, and the same pH conditions. In these tests, however, water was collected post-filter from the

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